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Mathematical modeling of radially propagating polymerization waves with the gel effect

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Abstract

Frontal polymerization (FP) is a method of manufacturing polymer via a self-propagating reaction wave. There are two types of FP processes: thermal and isothermal. In all previous works the two types of FP were studied separately. In this work we model a process in which both thermal and isothermal FP can occur, and demonstrate the transition from isothermal to thermal FP. Our model describes the radial propagation of an isothermal front from the lateral surface of a test tube toward the axis, which may give rise to the thermal mode of propagation due to the temperature build-up.

Keywords: Polymerization; Mathematical modeling; Isothermal frontal polymerization; Gel effect; Thermal frontal polymerization

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1. Introduction

Frontal polymerization is a process that converts monomer into polymer by means of a self-propagating wave. This front is a highly localized spatial reaction zone which propagates through a mixture of a monomer and an initiator, leaving the polymer in its wake.

Frontal polymerization studies began in 1972 [1]. This work was performed as a polymer analog to self-propagating high-temperature synthesis (SHS) [2], a combustion process used to make ceramics and intermetallic compounds. With methyl methacrylate as the monomer, the authors in [1,3–5] showed how the front velocity and the polymer composition are influenced by initiator species, initiator concentration and pressure change. Subsequent experimental work [6–9] showed that FP can occur in a variety of systems. Most of these experiments used liquid undiluted monomers. However, FP has also been carried out in systems with solid monomers [10,11], in dispersions [12], and in solutions [13]. Along with demonstrating the feasibility of FP with particular monomers, experimentalists have also focused on the synthesis of polymers with specific desired properties, e.g. functionally gradient polymeric materials [14], temperature-sensitive hydrogels [15], thermochromic composites [16,17], and conductive composites [18].

The chemical mechanism for FP is usually free-radical polymerization, which in the simplest case includes three kinetic steps: initiation, propagation, and termination. However, the process has also been successfully applied in epoxy curing [19], ring-opening metathesis [20], and thiol-ene polymerization [21], all of which have different chemistries. Mathematical models of FP have been developed in [22–38].

There are two modes of frontal polymerization: isothermal and thermal. Thermal frontal polymerization is usually initiated by applying a heat source at one end of a test tube. The temperature increase induces decomposition of the initiator into active radicals allowing polymer chain growth to begin. The chain growth which occurs in a narrow region with sufficiently high temperature, releases more heat which diffuses into an adjacent layer of reactants inducing decomposition of initiator there. In this way, a self-sustained reaction wave can travel through the mixture. The increase in temperature can be as high as 200 K. The propagation of the wave is hence due to the exothermic chemical reactions and heat diffusion. All of the above literature references are concerned with thermal frontal polymerization.

In an isothermal mode of polymerization, the propagation of the wave is due to the mass diffusion of the species and the gel effect. The reaction typically starts when a polymer seed, that is, a piece of polymer, is placed in contact with a solution of its monomer and an initiator. The monomer swells